

IAP20 Rec'd PCT/PTO 22 DEC 2005

PROPYLENE-STYRENE COPOLYMERISATION PROCESS

The present invention relates to a process for the production of a copolymer, in particular a copolymer comprising styrene units and propylene units. The copolymer produced according to the present method is generally a random copolymer which is crystalline and easily processible.

In the past, attempts have been made to produce random olefin polymers using metallocene catalysts. In Angew. Chem. Int. Ed. 1998, Vol. 37, No. 7, pages 922-925, Leclerc and Waymouth describe metallocene compounds having a cyclopentadiene ligand (Cp) and a fluorene ligand (Flu), which can be used in the copolymerisation of ethene and propylene. In particular, zirconium metallocene catalysts comprising unsubstituted Cp, 3-methyl Cp, 3-*tert*-butyl Cp and 3,4-dimethyl Cp ligands are disclosed.

Metallocene catalysts are known to be useful in various polymerisation processes. For example, in EP 0581236, specific metallocene catalysts are described as being useful for the production of isotactic polypropylene (iPP).

However, up to present methods for producing olefin-styrene copolymers are not entirely satisfactory, particularly in slurry processes. This is due to the nature of styrene, which is difficult to polymerise in this way. Styrene is very reactive, when compared with most other commonly used monomers (such as ethylene and propylene) and tends to polymerise with itself before any co-monomer can be incorporated into the polymer. Thus, previous attempts to produce styrene copolymers have succeeded only in producing mixtures of polystyrene with another polymer, or polystyrene with a very small co-monomer content. There is thus still a need for an improved method of forming olefin-styrene copolymers, especially random olefin styrene polymers where the styrene and its co-monomer are incorporated randomly (or quasi-randomly, such as in an alternating fashion) throughout the copolymer.

A further problem is that known random polymers have retained a large amount of solubles (extractables). These are low molecular weight highly copolymerised species. This was a problem with the use of first generation catalysts, such as chromium and Ziegler-Natta catalysts. The solubles migrate to the surface creating a haze in the films, which is a disadvantage for many uses particularly in the food and medical areas.

With a view to overcoming these problems, attempts were made to replace these catalysts with bis-indenyl metallocene catalysts. This led to much more homogeneous chain compositions. However, it proved difficult and expensive to produce pure racemic bis-indenyl catalysts, and even when this can be achieved, the pure catalysts unavoidably undergo some conversion to their meso derivatives. The meso derivative produces atactic polyolefins which are generally soluble/extractable as discussed above.

Accordingly, it is an object of the present invention to solve the problems associated with the above prior art. It is a further object of the present invention to provide an improved method for the formation of propylene-styrene copolymers, especially random and quasi-random copolymers, which polymers have improved properties, such as good crystallinity and easy processibility. It is also an object of the invention to produce propylene-styrene copolymers having good clarity and transparency characteristics, and a low solubles content. It is a further object of the present invention to provide an improved method for forming propylene-styrene copolymers having such improved properties.

Thus, the present invention provides a method for the production of a copolymer of styrene and propylene, which method comprises copolymerising styrene and propylene in the presence of a metallocene catalyst, wherein the metallocene catalyst comprises a metallocene having either formula (I):



wherein Cp comprises a cyclopentadienyl ring; Flu comprises a fluorenyl ring; R'' comprises a structural bridge imparting stereorigidity to the component; each R is the same or different and is an organic group; m is an integer of from 0-4; each R' is the same or different and is an organic group; n is an integer of from 0-8; M is a metal atom from group 4 of the Periodic Table or is vanadium; and each Q is a hydrocarbon having from 1-20 carbon atoms or is a halogen;

or formula (II):



wherein (FluR'_n), R'', M and Q are as defined here-above; X is a heteroatom from group 15 or group 16 of the Periodic Table and R^{\$} is hydrogen or a hydrocarbonyl having from 1 to 20 carbon atoms.

The methods of the present invention involve a process of copolymerisation. In the context of the present invention, copolymerisation means polymerising two or more olefin monomers, one of which being a styrene monomer, together in the same reaction zone under polymerisation conditions. It is preferred that the present method involves the copolymerisation of styrene with propylene to form a propylene-styrene copolymer. However, two, three or more further olefin monomers may be polymerised together with styrene in the present methods, if desired, to form, for example, a terpolymer.

The methods of the present invention are particularly advantageous, since they allow for the production of improved styrene-propylene copolymers, especially random copolymers, having good processibility, and high crystallinity and good optical properties, such as low haze and high transparency. The catalysts used

in the present invention have no meso form (they are single site catalysts) and do not suffer the problems of producing extractables, or low molecular weight product.

The present invention will now be described in further detail.

The substituents that may be present on the cyclopentadiene and fluorene rings (R and R' respectively) will now be described in more detail. The substituent or substituents are not particularly limited. The cyclopentadiene ring (Cp) may be unsubstituted, but is preferably at least mono-substituted. If desired, it may comprise one or more further substituents, provided that these further substituents do not adversely interfere with the ability of the present method to produce random olefin copolymers. The Cp ring may be substituted with the same substituent throughout, or with different substituents. The fluorene ring (Flu) may be substituted or unsubstituted and may also be substituted with the same substituent throughout, or with different substituents. Most preferably it is symmetrically substituted.

The substituents on the Cp and Flu rings are not particularly limited and may comprise any organic group and/or one or more atoms from any of groups 13, 14, 15, 16, 17 of the Periodic Table, such as a B, Si, C, N, P, O, or S atom or a halogen atom (e.g. F, Cl, Br or I).

When the substituent comprises an organic group, the organic group preferably comprises a hydrocarbon group. The hydrocarbon group may comprise a straight chain, a branched chain or a cyclic group. Independently, the hydrocarbon group may comprise an aliphatic or an aromatic group. Also independently, the hydrocarbon group may comprise a saturated or unsaturated group.

When the hydrocarbon comprises an unsaturated group, it may comprise one or more alkene functionalities and/or one or more alkyne functionalities. When the hydrocarbon comprises a straight or branched chain group, it may comprise one or more primary, secondary and/or tertiary alkyl groups. When the hydrocarbon comprises a cyclic group it may comprise an aromatic ring, an aliphatic ring, a heterocyclic group, and/or fused ring derivatives of these groups. The cyclic group may thus comprise a benzene, naphthalene, anthracene, indene, fluorene, pyridine, quinoline, thiophene, benzothiophene, furan, benzofuran, pyrrole, indole, imidazole, thiazole, and/or an oxazole group, as well as regioisomers of the above groups.

The number of carbon atoms in the hydrocarbon group is not especially limited, but preferably the hydrocarbon group comprises from 1-40 C atoms. The hydrocarbon group may thus be a lower hydrocarbon (1-6 C atoms) or a higher hydrocarbon (7 C atoms or more, e.g. 7-40 C atoms). The number of atoms in the ring of the cyclic group is not especially limited, but preferably the ring of the cyclic group comprises from 3-10 atoms, such as 3, 4, 5, 6 or 7 atoms.

The groups comprising heteroatoms described above, as well as any of the other groups defined above, may comprise one or more heteroatoms from any of groups 13, 14, 15, 16, 17 of the Periodic Table, such as a B, C, Si, N, P, O, or S atom or a halogen atom (e.g. F, Cl, Br or I). Thus the substituent may comprise one or more of any of the common functional groups in organic chemistry, such as hydroxy groups, carboxylic acid groups, ester groups, ether groups, aldehyde groups, ketone groups, amine groups, amide groups, imine groups, thiol groups, thioether groups, sulphate groups, sulphonic acid groups, and phosphate groups etc. The substituent may also comprise derivatives of these groups, such as carboxylic acid anhydrides and carboxylic acid halides.

In addition, any substituent may comprise a combination of two or more of the substituents and/or functional groups defined above.

Typically, the substituents are independently selected from an aryl group and a hydrocarbyl group having from 1-20 carbon atoms. The most preferred substituents are methyl groups or butyl groups. Other preferred substituents include Et, n-Pr, i-Pr, n-Bu, t-Bu, Me₃Si, R-O, cycloalkyl, and halogen.

In respect of the Cp ring, it is especially preferred that at least one group R comprises a bulky group of the formula ZR*₃ in which Z is an atom from group 14 of the Periodic Table and each R* is the same or different and is chosen from a hydrogen or a hydrocarbyl group having from 1-20 carbon atoms. When such an R group is present, it is also preferred that at least one further group R is present comprising a group of the formula YR#₃ in which Y is an atom from group 14 of the Periodic Table, and each R# is the same or different and is chosen from a hydrogen or a hydrocarbyl group having from 1-7 carbon atoms.

Regarding the position of the substituents, generally at least one group R is positioned on the cyclopentadienyl ring such that it is distal to the bridge R". However, in some embodiments of the invention at least one group R is positioned on the cyclopentadienyl ring such that it is proximal to the bridge R". It is particularly preferable that the cyclopentadienyl ring comprises a bulky substituent ZR*₃ distal to the bridge R" and a substituent YR#₃ proximal to the bridge and non-vicinal to ZR*₃. In some embodiments of the present invention, the cyclopentadienyl ring comprises a substituent ZR*₃ distal to the bridge R"; a substituent YR#₃ proximal to the bridge R" and non-vicinal to ZR*₃; and a further substituent YR#₃ proximal to the bridge and vicinal to ZR*₃. The cyclopentadienyl ring may also comprise two substituents ZR*₃, each distal to the bridge R", if desired.

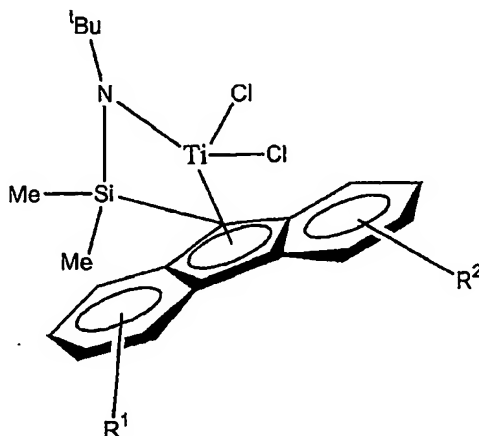
In a preferred embodiment, Z and Y in the above formulae independently comprise carbon or silicon. The catalyst compounds used in the present

methods are typically compounds in which ZR^*_3 is selected from $C(CH_3)_3$, $C(CH_3)_2Ph$, CPh_3 , and $Si(CH_3)_3$. It is particularly preferred that ZR^*_3 comprises $C(CH_3)_3$. In further preferred embodiments of the present invention, YR^*_3 comprises a methyl group or a trimethylsilyl group (TMS)

The substitution pattern of the fluorene ring (on both types of catalysts I and II) is not especially limited, provided that it does not adversely interfere with the copolymerisation method of the present invention. The fluorenyl ring is preferably symmetrically substituted. Most preferably both the 3- and the 6-position are substituted in catalysts of type (I), and of type (II). Alternatively the fluorenyl ring comprises a substituent at the 2-position and at the 7-position.

In respect of catalysts of type (II), it is preferred that the group X is an atom from group 15 of the Periodic Table, particularly N or P. When X is from group 16 it will be apparent that X is not further substituted. However, when X is from group 15, it will be apparent that X will be further substituted to make up the required valence of the N or P atom. In this instance, further substitution may be any hydrocarbon group already discussed above. Most preferably however, the group is a bulky group, such as a tertiary butyl group.

The catalysts of type (II) most preferably have the following structure:



wherein R^1 and R^2 are substituents at both the 2- and 7-positions, or both the 3- and 6-positions of the fluorenyl group, and are bulky groups of the formula ZR^*_3 in which Z is an atom from group 14 of the Periodic Table and each R^* is the same or different and is chosen from a hydrogen or a hydrocarbyl group having from 1-20 carbon atoms.

In the more preferred embodiments, R^1 and R^2 are both tBu groups. It is particularly preferred that these tBu groups are in the 3-position and the 6-position.

The type of bridge present between the rings in the above-described catalysts is not itself particularly limited. Typically R" comprises an alkylidene group having 1 to 20 carbon atoms, a germanium group (e.g. a dialkyl germanium group), a silicon group (e.g. a dialkyl silicon group), a siloxane group (e.g. a dialkyl siloxane group), an alkyl phosphine group or an amine group. Preferably, the substituent comprises a silyl radical or a hydrocarbyl radical having at least one carbon atom to form the bridge, such as a substituted or unsubstituted ethylenyl radical (e.g. $-CH_2CH_2-$). Most preferably R" is isopropylidene (Me_2C), Ph_2C , ethylenyl, or Me_2Si .

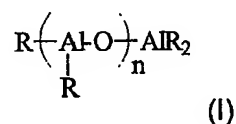
It is further preferred that the metallocene compounds used in the present invention are those wherein M is Ti, Zr, or Hf. Typically, the Q groups attached to the metal atoms are alkyl groups having from 1 to 6 carbon atoms, preferably methyl groups. Alternatively Q may be a halogen, such as Cl.

The further optional olefin employed in the present invention in addition to styrene and propylene is not particularly limited, and may be any olefin. Suitable olefins include ethylene, propylene, butene, pentene and hexene. Preferably the olefin is an alpha-olefin.

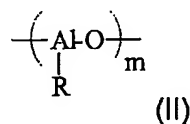
In addition to the above metallocene compound, the catalyst used in the present methods may comprise one or more activating agents capable of activating any one or more of the catalyst components. Typically, the activating agent comprises an aluminium- or boron-containing activating agent.

Suitable aluminium-containing activating agents comprise an alumoxane, an alkyl aluminium compound and/or a Lewis acid.

The alumoxanes that can be used in the present invention are well known and preferably comprise oligomeric linear and/or cyclic alkyl alumoxanes represented by the formula (I):



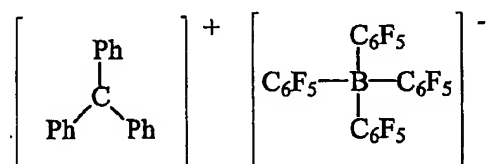
for oligomeric linear alumoxanes; and formula (II)



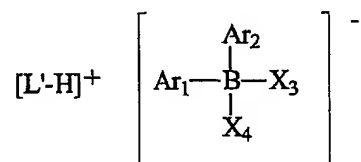
for oligomeric cyclic alumoxanes,

wherein n is 1-40, preferably 10-20; m is 3-40, preferably 3-20; and R is a C_1 - C_8 alkyl group, preferably methyl. Generally, in the preparation of alumoxanes from, for example, aluminium trimethyl and water, a mixture of linear and cyclic compounds is obtained.

Suitable boron-containing activating agents may comprise a triphenylcarbenium boronate, such as tetrakis-pentafluorophenyl-borato-triphenylcarbenium as described in EP-A-0427696:



or those of the general formula below, as described in EP-A-0277004 (page 6, line 30 to page 7, line 7):



Other preferred activating agents include hydroxy isobutylaluminium and a metal aluminoxinate. These are particularly preferred when at least one Q in the general formula for metallocenes comprises an alkyl group.

The catalyst systems employed in the present invention may be employed in any type of copolymerisation method, provided that the required catalytic activity is not impaired. In a preferred embodiment of the present invention, the catalyst system is employed in a solution polymerisation process, which is homogeneous, or a slurry process, which is heterogeneous. In a solution process, typical solvents include hydrocarbons having 4-7 carbon atoms such as heptane, toluene or cyclohexane. In a slurry process, it is necessary to immobilise the catalyst system on an inert support, particularly a porous solid support such as talc, inorganic oxides and resinous support materials such as polyolefin. Preferably, the support material is an inorganic oxide in its finely divided form.

Suitable inorganic oxide materials that are desirably employed in accordance with this invention include group 2, 4, 13 or 14 metal oxides such as silica, alumina and mixtures thereof. Other inorganic oxides that may be employed, either alone or in combination with the silica or alumina, are magnesia, titania, zirconia, and the like. Other suitable support materials, however, can be employed, for example, finely divided functionalised polyolefins such as finely divided polyethylene.

Preferably, the support is a silica support having a surface area of from 200-700 m²/g and a pore volume of from 0.5-3 ml/g.

The amount of activating agent and metallocene usefully employed in the preparation of the solid support catalyst can vary over a wide range. Preferably, the activating agent to transition metal mole ratio is in the range between 1:1 and 100:1, preferably in the range 5:1 and 50:1.

The order of addition of the catalyst components and activating agent to the support material can vary. In accordance with a preferred embodiment of the present invention activating agent dissolved in a suitable inert hydrocarbon solvent is added to the support material slurried in the same or other suitable hydrocarbon liquid and thereafter a mixture of the catalyst components is added to the slurry.

Preferred solvents include mineral oils and the various hydrocarbons which are liquid at reaction temperature and which do not react with the individual ingredients. Illustrative examples of the useful solvents include the alkanes such as pentane, iso-pentane, hexane, heptane, octane and nonane; cycloalkanes such as cyclopentane and cyclohexane, and aromatics such as benzene, toluene, ethylbenzene and diethylbenzene.

Preferably, the support material is slurried in toluene and the catalyst components and activating agent are dissolved in toluene prior to addition to the support material.

The present invention further provides use of a metallocene catalyst for producing a copolymer of styrene and propylene, wherein the metallocene catalyst comprises a metallocene having either formula (I):



wherein Cp comprises a cyclopentadienyl ring; Flu comprises a fluorenyl ring; R'' comprises a structural bridge imparting stereorigidity to the component; each R is the same or different and is an organic group; m is an integer of from 0-4; each R' is the same or different and is an organic group; n is an integer of from 0-8; M is a metal atom from group 4 of the Periodic Table or is vanadium; and each Q is a hydrocarbon having from 1-20 carbon atoms or is a halogen;

or formula (II):



wherein (FluR'_n), R'', M and Q are as defined here-above; R^s is hydrogen or a hydrocarbyl group having from 1-20 carbon atoms, X is a heteroatom from group 15 or group 16; and wherein the FluR'_n group is preferably symmetrically substituted.

Also provided is a copolymer, obtainable according to the methods defined above. The copolymer is preferably a styrene-propylene copolymer in which there is reasonably even distribution of the styrene and propylene units

throughout each polymer molecule so that large blocks of each monomer unit do not form. Without being bound by theory, it is thought that this provides the polymer with its advantageous crystallinity, optical properties and processibility. The copolymers obtained according to the present invention have a styrene content of from 2 to 50 wt %, preferably of from 5 to 25 wt%.

Applications for which the polymers of the present invention are particularly suited include films and impact copolymers.

The present invention will now be described in further detail, by way of example only, with reference to the following specific embodiments.

List of Figures.

Figure 1 represents the ^1H NMR spectra of complex $\{\text{tBu}_2\text{-C}_{13}\text{H}_6\text{-SiMe}_2\text{-N}^{\text{tBu}}\}\text{TiCl}_2$ in benzene- d_6 at a temperature of 20 °C and at 200 MHz.

Figure 1 represents the ^1H NMR spectra of complex $\{\text{tBu}_2\text{-C}_{13}\text{H}_6\text{-SiMe}_2\text{-N}^{\text{tBu}}\}\text{TiMe}_2$ in benzene- d_6 at a temperature of 20 °C and at 200 MHz.

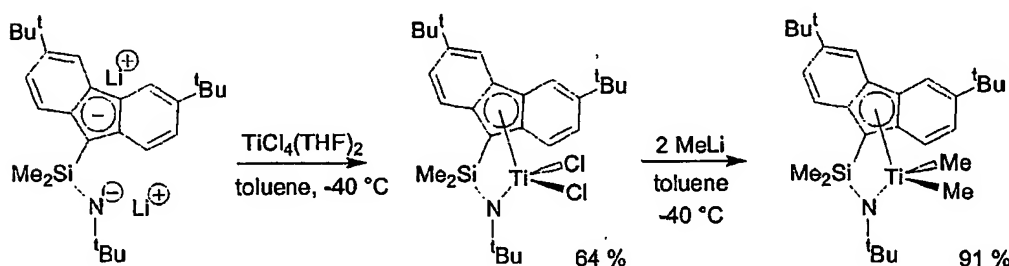
Figure 3 represents the molecular structure of complex $\{\text{tBu}_2\text{-C}_{13}\text{H}_6\text{-SiMe}_2\text{-N}^{\text{tBu}}\}\text{TiMe}_2$.

Figure 4 represents the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the propylene-styrene copolymer in CDCl_3 at a temperature of 60 °C.

Examples.

Preparation of components $\{\text{tBu}_2\text{-C}_{13}\text{H}_6\text{-SiMe}_2\text{-N}^{\text{tBu}}\}\text{TiCl}_2$ (1) and $\{\text{tBu}_2\text{-C}_{13}\text{H}_6\text{-SiMe}_2\text{-N}^{\text{tBu}}\}\text{TiMe}_2$ (2).

The dichloro complex $\{3,6\text{-}^t\text{Bu}_2\text{C}_{13}\text{H}_6\text{SiMe}_2\text{N}^t\text{Bu}\}\text{TiCl}_2$ (**1**) was prepared with 64% yield according to the procedure published by Razavi, A. et al. in *J. Organomet. Chem.* **2001**, 621, 267. $\text{TiCl}_4(\text{THF})_2$ was reacted with 1 equivalent of the dilithium salt of the fluorenyl-amido ligand represented in scheme 1, in toluene and at a temperature of $-40\text{ }^\circ\text{C}$.



The new corresponding dialkyl complex $\{3,6\text{-}^t\text{Bu}_2\text{C}_{13}\text{H}_6\text{SiMe}_2\text{N}^t\text{Bu}\}\text{TiMe}_2$ (**2**) was obtained as follows. 170 mg (0.339 mmol) of complex (**1**) in 30 mL of toluene at a temperature of $-40\text{ }^\circ\text{C}$ were added under vigorous stirring to 2 equivalents of MeLi (0.38 mL of a 1.6 M solution in Et_2O , or 0.677 mmol). The reaction mixture was allowed to warm to room temperature and then stirred for 12 h. The brown-orange solution was decanted from precipitate and volatiles were removed in vacuum to give 0.15 g of complex **2** as an orange solid with a yield of 91%. Orange-yellow crystals of complex **2** suitable for X-ray analysis were grown from a pentane solution.

The ^1H NMR spectra of complexes **1** and **2** are presented respectively in Figures 1 and 2 and show the usual resonance pattern of for symmetrically coordinated complexes. The solid state structure of complex **2** is reminiscent to that of its zirconium analogue and is represented in Figure 3.

The ^1H NMR (benzene- d_6 , 200 MHz, 20 °C) spectrum of complex (1) was as follows: δ 8.00 (d, 2H, $J_{\text{HH}} = 1.5$ Hz, 4,5-Flu), 7.84 (d, 2H, $J_{\text{HH}} = 8.6$ Hz, 1,8-Flu), 7.36 (d, 2H, $J_{\text{HH}} = 1.5, 8.6$ Hz, 2,7-Flu), 1.50 (s, 9H, NCCH_3), 1.32 (s, 18H, $\text{CCH}_3(\text{Flu})$), 0.70 (s, 6H, SiCH_3).

The ^1H NMR (benzene- d_6 , 200 MHz, 25 °C) spectrum of complex (2) was as follows: δ 8.23 (d, 2H, $J_{\text{HH}} = 1.6$ Hz, 4,5-Flu), 7.72 (d, 2H, $J_{\text{HH}} = 8.7$ Hz, 1,8-Flu), 7.33 (d, 2H, $J_{\text{HH}} = 1.6, 8.7$ Hz, 2,7-Flu), 1.46 (s, 9H, NCCH_3), 1.37 (s, 18H, $\text{CCH}_3(\text{Flu})$), 0.81 (s, 6H, SiCH_3), 0.07 (s, 6H, CH_3).

The $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6 , 75 MHz, 25 °C) spectrum of complex (2) was as follows: δ 133.5, 128.1, 127.7, 127.3, 126.9, 118.3 (C-1, -2, -3, -4, -5, -6, -7, -8), 79.1 (C-9), 58.2 (NCCH_3), 55.5 (CH_3), 34.3 (NCCH_3), 34.8 (Flu-CCH_3), 31.5 (Flu-CCH_3), 5.5 (SiCH_3).

Calculated for $\text{C}_{29}\text{H}_{49}\text{NSiTi}$: C, 71.43; H, 10.13; N, 2.87. Mr, 487.659. Found: C, 69.81; H, 10.37; N, 2.64.

Complexes 1 and 2 were activated either with methyalumoxane (MAO) or with the borane compound $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ (Turner) as indicated in Table I.

Two additional complexes were tested:

$\{3,6\text{-}^t\text{Bu}_2\text{C}_{13}\text{H}_6\text{SiPh}_2\text{N}^t\text{Bu}\}\text{TiCl}_2$ (4) and

complex $\text{CpTiCl}_3(\text{THF})$ (5) that is known in the polymerisation of styrene.

Typical procedure for copolymerisation of styrene and propylene.

A glass high-pressure reactor was charged with 50 mL of freshly distilled solvent under argon flash. The reactor was loaded with styrene and propylene as described in Table I, at atmospheric pressure and a solution of catalyst in 5 mL of toluene was injected by syringe. Mechanic stirring at 1,000 rpm was started and the required pressure of gas (typically 5 atm) was maintained constant. The reaction was quenched by adding 2 mL of a 10 % solution of HCl in methanol.

The polymer formed was precipitated by adding of 300 mL of methanol. The precipitate was then washed and dried in vacuum. The polymerisation conditions and results are displayed in Table I.

TABLE I.

Com plex	Activ. agent	Al/Ti or B/Ti	[Ti] μmol/L	[Styr] mol/L	P _{prop} atm	T °C	t min	yield g	M _w kDa	M _w /M _n
1	MAO	500	378	4.3	5	25	50	2.5	35	1.58
1	MAO	500	378	4.3	5	25	50	<0.5	-	-
1	MAO	500	378	4.3	5	25	50	<0.5	-	-
1^a	MAO	500	378	4.3	5	25	50	0.676	40	1.58
1^b	MAO	500	378	4.3	5	25	50	0.756	-	-
1	MAO	500	378	4.3	5	60	120	0.613	-	-
1	MAO	500	378	4.3	5	25	120	<0.5	-	-
1	MAO	500	370	5.0	3	60	140	0.54	-	-
1	MAO	500	370	8.6	5	60	180	1.023	54	21.1
1	"dried" MAO	500	378	4.3	5	25	50	<0.5	-	-
2^c	Turner	3	378	4.3	5	50	65	0.32	-	-
2^d	Turner	3	378	4.3	5	50	65	0.25	-	-
2^e	MAO	500	370	4.3	5	25	150	2.0	?	-
2^e	MAO	500	370	4.3	5	60	240	1.2	?	-
2^e	MAO	500	370	0.86	5	25	160	8.7	?	-
1+5^f	MAO	500	378	4.3	5	25	60	3.15	26	1.84
1+5^f	MAO	500	378	8.6	5	25	60	8.2	308	bimod.
1+5^{d,f}	Turner	3	378	4.3	5	25	60	3.0	17	1.97
4+5^g	MAO	500	378	4.3	5	25	65	1.24	-	-

^a half of MAO introduced into the reactor, half to prepare catalyst

^b all MAO injected into the reactor

^c [Al(ⁱBu)₃]/[Ti] = 1000

^d [Al(ⁱBu)₃]/[Ti] = 50

^e solvent = cyclohexane (50 mL)

^f Complexes **1** and **5** were used in a 3 to 1 ratio.

^g Complexes **4** and **5** were also used in a 3 to 1 ratio.

The copolymers according to the present invention have only a minor fraction that is soluble in CHCl₃ and tetrahydrofuran (THF) at room temperature. Both the soluble fraction at room temperature in CDCl₃ and the whole sample soluble at

130 °C in $C_6H_4Cl_2$ show a low incorporation percentage of styrene of 4 to 5 mol% as determined by NMR. They have a low molecular weight and a narrow polydispersity. The polydispersity is defined as the ratio M_w/M_n of the weight average molecular weight M_w to the number average molecular weight M_n . The molecular weights were determined by Gel Permeation Chromatography (GPC). The microstructure of such copolymer, as determined by $^{13}C\{^1H\}$ NMR of the whole sample at 135 °C in $C_6H_4Cl_2$, is consistent with sPP sequences ($r > 92\%$) with single styrene units randomly distributed along the polymeric chain. The Differential Scanning Calorimetry (DSC) analysis for such copolymers showed no distinct melting point.

Rather promising results were obtained using complex **2** in combination with MAO as activating agent. This combination was preferred because of the enhanced stability of the dialkyl complex **2** as compared to the significantly less stable dichloro complex **1**, thereby excluding the presence of possible contaminants in complex **1**, that could be detrimental to the catalyst's performance. At the same time, MAO can play a double role in this system:

- (i) It can activate the pre-catalyst to generate active cationic species;
- (ii) It can act as a scavenger.

The increase of polymerisation temperature had a detrimental effect on the activity of the system, possibly by destroying the active species. The presence of a large excess of styrene with respect to propylene in the solution inhibited markedly the polymerisation and did not result in an increase of the styrene content in the copolymer. Copolymerisation carried out with a low styrene feed resulted on the contrary in improved activity.

All these polymers have poor solubility in $CDCl_3$ and THF at room temperature. The $^{13}C\{^1H\}$ NMR spectrum of the propylene-styrene copolymer in $CDCl_3$ at 60 °C is represented in Figure 4. It features a major set of signals assigned to sPP units and low intensity signals that correspond to styrene units, suggesting the same microstructure.

A few polymerisation procedures were carried out by adding to complex **1**, complex **5** that is known to catalyse the syndiospecific polymerisation of styrene when activated by MAO. The respective amounts of complexes **1** and **5** were in a ratio of 3 to 1. The polymerisation conditions and results are reported in Table I. The polymers recovered had poor solubility in CDCl₃ and THF at room temperature and they were largely soluble (about 80 %) in hot CHCl₃. The fraction that was not soluble in CHCl₃ was a mixture of syndiotactic polystyrene (sPS) and of syndiotactic polypropylene (sPP) as determined by DSC. The soluble fraction was analysed by GPC: it revealed a low molecular weight and a narrow polydispersity. The styrene content as determined by ¹H NMR spectroscopy gave a styrene content of about 18 mol%. Increasing the styrene content led to polymer products also composed of homopolymers of sPS and sPP.